A General Method for Calculating Elastic Moduli of Helical Polymer Chains in Crystals; Application to Poly(Oxymethylene)

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ABSTRACT: A new general method was derived for calculating elastic moduli of isolated polymer-chains and of polymer-chains in crystals. Equations for elastic moduli were written with the B submatrices as used in normal coordinate treatments. The new method was applied for calculating the elastic moduli of (poly)oxymethylene chains in trigonal and orthorhombic crystals.

KEY WORDS   Polymer / Young's Modulus / Elastic Modulus / Intrachain Potential / Helical Structure / Poly(Oxymethylene) /

Force fields of chain-polymer crystals are much more anisotropic than those molecular of crystals, and the intrachain restoring force along the chain direction is much stronger than interchain restoring forces. Because of this strong anisotropy of force fields in chain-polymer crystals, the elastic modulus in the direction of the chain axis may be reasonably treated with the single-chain approximation.

Elastic moduli of polymer chains were previously calculated by Meyer and Lotmar,[1] Lyons[2], and Treloar[3], with the use of bond-stretching and bond-angle bending force constants. However, general methods for calculating elastic moduli of helical polymer chains were derived by Shimanouchi *et al.*[4] and by Miyazawa[5].

The repeating regularity of a helical polymer-chain is characterized with the unit translation (d) along the helix axis and the unit twist (θ) about the axis (Figure 1),[6-8] while the intrachain potential is usually expressed with bond-stretching (Δr), angle-bending ($\Delta \phi$) and internal-rotation coordinates ($\Delta \tau$). Accordingly, Shimanouchi, Asahina and Enomoto[4] derived the equations for elastic moduli from the relation[6,7] between the unit translation (d) and intramolecular parameters (r, ϕ, and τ). On the other hand, Miyazawa[5] derived the equations for elastic moduli and elastic strains from the relation between intramolecular parameters and helical parameters (ρ_i, d_{ij}, and θ_{ij}).[7] In these previous studies, elastic moduli of isolated polymer-chains were calculated without the restriction of $\Delta\theta = 0$.

However, if a polymer crystal is subject to a homogeneous deformation, translational symmetries of the three-dimensional crystal lattice are reserved and constituent polymer-chains are deformed so that the unit translation is changed ($\Delta d \neq 0$) but the unit twist is kept constant ($\Delta \theta = 0$). Accordingly, for calculating elastic moduli of polymer-chains in crystals, previous methods[4,5] can not be applied.

In the present study, therefore, a new general method is derived for calculating elastic moduli of isolated polymer-chains ($\Delta\theta \neq 0$) and of polymer-chains in crystals ($\Delta\theta = 0$). Equations for elastic moduli are written with B submatrices[9] as used for normal-vibration treatments of helical polymer chains.

HOMOGENEOUS DEFORMATION OF POLYMER CHAINS

Elastic deformation of an isolated polymer-chain is assumed to be uniform under a tension along the chain axis. A homogeneous deformation of a helical chain may be described with changes in unit translation (Δd) and in unit twist ($\Delta\theta$). Accordingly, the external-strain vector $\widetilde{U} = [u_1 \ u_2]$ may be defined as

$$u_1 = u_d = \Delta d/d$$
$$u_2 = u_\theta = \Delta \theta \tag{1}$$

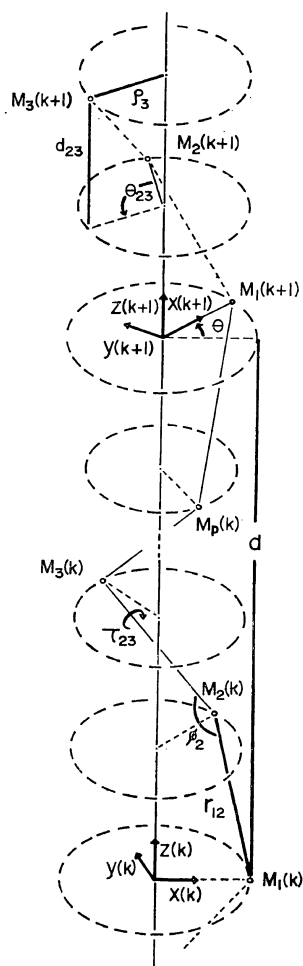where a tilde denotes the transpose of a matrix.

Figure 1. Helix parameters and intramolecular parameters.

For treating elastic moduli of isolated polymer-chains, u_1 and u_2 are both used as external strains. However, for treating elastic moduli of polymer chains in crystals, only u_1 is used as the external strain and rows and columns associated with u_2 should be dropped in succeeding equations.

ELASTIC MODULI OF HELICAL POLYMER CHAINS

For describing displacements of chain atoms under a homogeneous deformation, right-handed Cartesian coordinates $\tilde{x}(k) = [x(k)\ y(k)\ z(k)]$ of the k-th repeat unit are defined as shown in

Figure 1; the $z(k)$ axis rests on the helix axis. The Cartesian displacement vector $X(k)$ of the k-th unit with p atoms $[M_1(k)\ M_2(k)\ldots M_p(k)]$ are given as,

$$\tilde{X}(k) = [\varDelta x_1(k)\varDelta y_1(k)\varDelta z_1(k)\varDelta x_2(k)\varDelta y_2(k)\varDelta z_2(k)$$
$$\ldots \varDelta x_p(k)\varDelta y_p(k)\varDelta z_p(k)]$$
(2)

The displacement vector $X(k)$ of the k-th unit is transformed into the vector $X(k + 1)$ of the $(k + 1)$-th unit by the screw operation with the unit translation (d) and the unit twist (θ).

For a homogeneous deformation of an isolated chain, atomic displacements are related with external strains,

$$\varDelta x_i(k + m) - \varDelta x_i(k) = -y_i m\varDelta\theta = -my_iu_2$$
$$\varDelta y_i(k + m) - \varDelta y_i(k) = x_i m\varDelta\theta = mx_iu_2$$
$$\varDelta z_i(k + m) - \varDelta z_i(k) = m\varDelta d = mdu_1$$
(3)

where x_i and y_i are coordinates of the i-th atom. Eq. 3 may be rewritten in matrix forms,

$$X(k + m) - X(k) = mTU$$
(4)

where T is given as

$$\tilde{T} = [\tilde{t}_1\ \tilde{t}_2\ \ldots\tilde{t}_p]$$
(5)

$$t_i = \begin{bmatrix} 0 & -y_i \\ 0 & x_i \\ d & 0 \end{bmatrix}$$
(6)

External strains (u_1 and u_2) of a homogeneous deformation are accompanied with atomic displacements of each unit so that the potential energy is minimized or, in other words, the internal stresses vanish. Defining internal strains ($\boldsymbol{\xi}$) as $X(0)$, the atomic displacements $X(m)$ of the m-th repeat unit may be expressed as

$$X(m) = \boldsymbol{\xi} + mTU$$
(7)

The potential energy (harmonic terms) of a polymer chain per unit volume may be expressed in terms of internal coordinates,

$$2V = (1/NAd) \sum_{k,m} \tilde{R}(k + m)F(k)R(m)$$
(8)

where N is the number of repeat units, A is the cross section per molecular chain, $R(m)$ is the internal coordinate vector of the m-th repeat unit, and $F(k)$ is the potential energy submatrix associated with $\tilde{R}(k + m)$ and $R(m)$, and

$$F(-k) = \tilde{F}(k) \qquad (9)$$

For a homogeneous deformation, internal coordinates of all the units (m) are common $R(m) = R$. Accordingly, the potential energy per unit volume may be rewritten as

$$2V = (1/Ad) \sum_k \tilde{R} F(k) R = (1/Ad) \tilde{R} F_0 R \quad (10)$$

where

$$F_0 = \sum_k F(k) \qquad (11)$$

For a helical polymer chain, the internal coordinates $R(k)$ and Cartesian displacement coordinates $X(k)$ of the k-th repeat unit are transformed into $R(k+1)$ and $X(k+1)$, respectively, of the $(k+1)$-th unit by the operation of screw-rotation. Accordingly the B matrix for a helical polymer is expressed in terms of the $B(m)$ sub-matrices,[9]

$$(2Ad)V = \tilde{\tilde{\xi}} \tilde{B}_0 F_0 B_0 \xi + \tilde{\tilde{\xi}} \tilde{B}_0 F_0 B_u U$$
$$+ \tilde{U} \tilde{B}_u F_0 B_0 \xi + \tilde{U} \tilde{B}_u F_0 B_u U$$
$$= \tilde{\tilde{\xi}} F_\xi \xi + 2 \tilde{\tilde{\xi}} F_{\xi u} U + \tilde{U} F_u U \qquad (17)$$

where

$$F_\xi = \tilde{B}_0 F_0 B_0 \qquad (18)$$
$$F_u = \tilde{B}_u F_0 B_u \qquad (19)$$
$$F_{\xi u} = \tilde{B}_0 F_0 B_u \qquad (20)$$

Under a given external strain (U), the internal strains (ξ) are derived from the condition of minimizing potential energy (V) or from the condition of null internal stresses ($\partial V/\partial \xi_i = 0$).

$$F_\xi \xi + F_{\xi u} U = 0 \qquad (21)$$
$$\xi = -F_\xi^{-1} F_{\xi u} U \qquad (22)$$

The singularity of the F_ξ matrix will be discussed

	$\ldots \tilde{X}(k-m) \ldots \tilde{X}(k-1)$	$\tilde{X}(k)$	$\tilde{X}(k+1) \ldots$	$\tilde{X}(k+m) \ldots$
.	$\ldots$. $\ldots$.	.	. $\ldots$.	$\ldots$
$R(k-1)$	$\ldots B(m-1) \ldots B(0)$	$B(-1)$	$B(-2) \ldots B(-m-1) \ldots$	
$R(k)$	$\ldots B(m) \quad \ldots B(1)$	$B(0)$	$B(-1) \ldots B(-m)$	
$R(k+1)$	$\ldots B(m+1) \ldots B(2)$	$B(1)$	$B(0) \quad \ldots B(-m+1) \ldots$	
.	$\ldots$. $\ldots$.	.	. $\ldots$.	$\ldots$ (12)

In general, the internal coordinates $R(k)$ are related to the Cartesian displacement coordinates $X(m)$ as,

$$R(k) = \sum_m B(m) X(k-m) \qquad (13)$$

From Eqs. 7 and 13, uniform internal displacements (R) may be written with internal (ξ) and external strains (U),

$$R = \sum_m B(m) X(-m) = \sum_m B(m)[\xi - mTU]$$
$$= B_0 \xi + B_u U \qquad (14)$$

where

$$B_0 = \sum_m B(m) \qquad (15)$$
$$B_u = -[\sum_m m B(m)]T \qquad (16)$$

Substituting Eq. 14 into Eq. 10, the potential energy (V) is given as

later. The uniform deformations (R) of internal coordinates are then derived from Eqs. 14 and 22.

$$R = (B_u - B_0 F_\xi^{-1} F_{\xi u})U \qquad (23)$$

The potential energy (V) is now expressed in terms of external strains (U).

$$2V = (1/Ad)\tilde{U}(F_u - \tilde{F}_{\xi u} F_\xi^{-1} F_{\xi u})U = \tilde{U} C U \quad (24)$$

where C is the elastic constant matrix as given by

$$C = (1/Ad)(F_u - \tilde{F}_{\xi u} F_\xi^{-1} F_{\xi u}) \qquad (25)$$

External stress parameters, $f_i (= \partial V/\partial u_i)$, are related to the external strain parameters as,

$$f = CU \qquad (26)$$

or alternately

$$U = C^{-1} f = S f \qquad (27)$$

where $S (= C^{-1})$ is the compliance matrix.

From Eqs. 22, 23, and 27, the internal strains

(ξ) and the internal coordinate displacements (R) under given external stresses (f) are given as,

$$\xi = -F_\xi^{-1}F_{\xi u}Sf \tag{28}$$

$$R = (B_u - B_0 F_\xi^{-1}F_{\xi u})Sf \tag{29}$$

Isolated Polymer Chains

The elastic modulus (E) along the chain axis is defined as,

$$E = \frac{1}{(\partial u_d/\partial f_d)}. \tag{30}$$

Under a homogeneous deformation of an isolated polymer chain ($u_2 \neq 0$),

$$\partial u_d/\partial f_d = S_{11} \tag{31}$$

and, accordingly the elastic modulus is given as,

$$E = \frac{1}{S_{11}} \tag{32}$$

Polymer Chains in Crystal

Under a homogeneous deformation of a polymer crystal, the unit translation is changed ($u_1 \neq 0$) but the unit twist is kept constant ($u_2 = 0$). Then,

$$f_d = C_{11}u_d \tag{33}$$

and accordingly the elastic modulus of helical polymer chains in crystal is given as

$$E = C_{11} \tag{34}$$

SINGULARITY OF F_ξ MATRIX

The F_ξ matrix of Eq. 18 is the potential energy matrix for infinitesimal atomic displacements totally symmetric with respect to the operations of screw-rotations. Among totally symmetric displacements of chain atoms, there are two overall displacements, namely the translation along the chain axis and the rotation about the chain axis. Accordingly, the F_ξ matrix has two null eigenvalues corresponding to the overall translation and rotation. Since the F_ξ matrix is singular, the F_ξ^{-1} matrix will be defined as follows:

The F_ξ matrix is diagonalized by the orthogonal transformation.

$$\xi = L\eta$$

$$\tilde{L}F_\xi L = \Lambda \tag{35}$$

where L is the eigenvector matrix ($\tilde{L} = L^{-1}$) and

Λ is the eigenvalue matrix with two null diagonal elements. Since the two null eigenvalues are due to the overall translation and rotation, the η coordinate vector is partitioned into two subvectors, η^* and η°, which are the η coordinates for the $3p-2$ genuine internal motions and for the overall translation and rotation, respectively. Accordingly, the eigenvector matrix L is also partitioned into L^* [$3p \times (3p - 2)$] and L° ($3p \times 2$), and the eigenvalue matrix Λ is factored into the Λ^* matrix with $3p-2$ nonzero diagonal elements and a zero matrix (0).

$$\eta = \begin{bmatrix} \eta^* \\ \eta^\circ \end{bmatrix} \quad L = [L^* \, L^\circ] \quad \Lambda = \begin{bmatrix} \Lambda^* & 0 \\ 0 & 0 \end{bmatrix}$$

$$\xi = L^*\eta^* + L^\circ\eta^\circ \tag{36}$$

For the new matrices L^* and Λ^*, the following relations are derived:

$$\tilde{L}^*F_\xi L^* = \Lambda^* \tag{37}$$

$$L^*\Lambda^*\tilde{L}^* = F_\xi \tag{38}$$

$$\tilde{L}^*L^* = E \quad [(3p-2)\times(3p-2) \text{ unit matrix}] \tag{39}$$

$$\tilde{L}^\circ F_\xi L^\circ = 0 \tag{40}$$

$$\tilde{L}^\circ F_\xi L^* = 0 \tag{41}$$

The second term ($L^\circ\eta^\circ$) on the right side in Eq. 36 is due to the overall translation and rotation, and is redundant in treating the potential energy associated with elastic deformations,

$$\xi = L^*\eta^* \tag{42}$$

Eq. 42 is now substituted into Eq. 21, yielding

$$F_\xi L^*\eta^* + F_{\xi u} U = 0 \tag{43}$$

Multiplication by $\tilde{L}^*$ from the left side gives

$$\Lambda^*\eta^* + \tilde{L}^*F_{\xi u} U = 0$$

$$\eta^* = -(\Lambda^*)^{-1}\tilde{L}^*F_{\xi u}U \tag{44}$$

From Eqs. 42 and 44,

$$\xi = -L^*(\Lambda^*)^{-1}\tilde{L}^*F_{\xi u}U \tag{45}$$

The atomic displacements (ξ) given by Eq. 45 are independent of the overall translation and rotation (Eqs. 44 and 45 may also be derived from the property of the B matrix $B_0 L^\circ = 0$). Comparing Eq. 45 with Eq. 22, the F_ξ^{-1} matrix may now be defined as

$$F_\xi^{-1} = L^*(\Lambda^*)^{-1}\tilde{L}^* \tag{46}$$

The matrix products $F_\xi^{-1}F_\xi$ and $F_\xi F_\xi^{-1}$ are not unit matrices. However, the following equations are derived from Eqs. 37–39 and 46:

$$F_\xi F_\xi^{-1}F_\xi = F_\xi \qquad (47)$$

$$F_\xi^{-1}F_\xi F_\xi^{-1} = F_\xi^{-1} \qquad (48)$$

ELASTIC MODULUS OF POLY(OXYMETHYLENE)

Poly(oxymethylene) (POM) has been found to exist in two crystalline forms, namely trigonal and orthorhombic. The molecular chain in the trigonal POM crystal takes a 9/5 helix with nine repeat units (CH_2O) and five turns per fiber period, while the molecular chain in the orthorhombic POM crystal takes a 2/1 helix with two units and one turn per fiber period. For the trigonal POM crystal, the elastic modulus in the direction of the chain axis was measured as 0.053 mdyne/Å^2 by Sakurada et al.[11]

The elastic moduli of POM chains were calculated with the general method of the present study. The structure parameters used in calculations are bond lengths of $r(\text{C–O}) = 1.42\text{Å}$ and $r(\text{C–H}) = 1.09\text{Å}$, tetrahedral valence angles, and internal-rotation angles $\tau(\text{C–O}) = 76°8'$ for the 9/5 helix and $\tau(\text{C–O}) = 60°0'$ for the 2/1 helix. The unit translations are $d = 1.866\text{Å}$ for the 9/5 helix and $d = 1.640\text{Å}$ for the 2/1 helix. The cross sections per molecular chain are $A = 17.31$ Å^2 for the 9/5 helix[12] and $A = 18.25\text{Å}^2$ for 2/1 helix[13]. The intrachain potential constants were refined previously,[14] by the method of least squares, with reference to the observed vibrational frequencies of the trigonal POM crystal at room temperature.[15,16] Calculated results are summarized in Table I.

Under a homogeneous deformation of a polymer crystal, constituent polymer chains are deformed with the condition of $\Delta\theta = 0$ and the elastic modulus of the 9/5 helical chain in the trigonal crystal is calculated as 0.095 mdyne/Å^2, as compared with the experimental value of 0.053 mdyne/Å^2. The elastic modulus of the 2/1 helical chain in the orthorhombic crystal is calculated as 0.048 mdyne/Å^2, although the experimental value is not available.

The 9/5 helical chain of trigonal POM is calculated to be much stiffer than the 2/1 helical

Table I. Changes in helix parameters (ρ, d and θ) and intramolecular parameters (r, ϕ and τ)[a] accompanying the chain-extension of POM through 1%

	Trigonal (9/5 helix)	Orthorhombic (2/1 helix)
$\Delta\rho_O$	−0.57	−0.51
$\Delta\rho_C$	−0.32	−0.27
Δd_{CO}	0.93	0.82
$\Delta\theta_{CO}$	0	0
$\Delta r(\text{C–O})$	0.10	0.03
$\Delta\phi(\text{C–O–C})$	1.17	0.82
$\Delta\phi(\text{O–C–O})$	0.83	0.57
$\Delta\tau(\text{C–O})$	0.89	0.84

[a] $\Delta\rho$, Δd, and Δr are given in Å/100 and $\Delta\theta$, $\Delta\phi$, and $\Delta\tau$ are given in radian/100.

chain of orthorhombic POM; the force required to stretch a chain through 1% is calculated as 0.0170 mdyne for the 9/5 helical chain which is twice as strong as the force (0.0088 mdyne) for the 2/1 helical chain. This difference in stiffness is due to the difference in chain-conformation; the internal-rotation angle is 76° for the 9/5 helical chain and 60° for the 2/1 helical chain. Possibly, the elastic modulus in the direction of the chain axis is fairly sensitive to chain conformations of helical polymers.

Finally it may be remarked that the calculated elastic moduli of isolated POM chains ($\Delta\theta \neq 0$) are much smaller than those of POM chains in crystals ($\Delta\theta = 0$); the calculated values of $E(\Delta\theta \neq 0)$ are as small as 0.040 mdyne/Å^2 for the 9/5 helical chain and as 0.019 mdyne/Å^2 for the 2/1 helical chain. However, for trigonal POM crystal at room temperature, the X-ray study by Sakurada et al.[11] indicates that the helix parameter θ does not change under stress and within the time scale of X-ray measurements. Accordingly, except for polymers with planar main chains, the elastic moduli of polymer chains previously calculated with the condition of $\Delta\theta \neq 0$ should be recalculated with the new condition of $\Delta\theta = 0$.

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